Grinders for Mulling Infrared Microsamples. Jesse S. Ard, Eastern Regional Research Laboratory, Philadelphia 18, Pa.

A VIBRATION grinder of exceptional simplicity was developed (*1*) for mulling a series of irreplaceable microsamples, and has proved satisfactory over several years of service. Mulling on a micro basis with this apparatus has been so convenient that the method has replaced all others for crystalline substances in the author's work, even when an abundant sample is available. Microsamples may also be ground with a reversed drill.

Mulls may be prepared with a mortar and pestle (*5*), by mashing between the cell windows (*3*), and by rotating cones (*6*); and methods developed for tissue mincing (*10*) are readily adaptable to this purpose. Many substances are soft enough to be mulled on a cell window with a toothpick. Cotton, representative of particularly difficult substances, was reported to give a suitable mull preparation after grinding in a vibratory ball mill, and this was regarded as more effective in this special case than the use of ultrasonic energy or a Waring Blendor (*4*). As an alternative to mulling, one may use films deposited by vacuum sublimation (*2*) or from solvents selected for favorable depositing characteristics (*6*). Samples admixed with potassium bromide (*8*, *9*) or polyethylene (*7*) may be compressed into appropriate sections.

VIBRATION APPARATUS AND METHOD

The apparatus, Figure 1, consists of a commercial holder to vibrate small tools, and a specially constructed hammer and anvil.

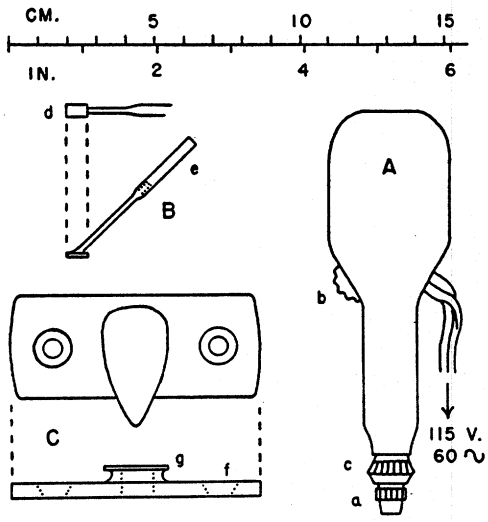

Figure 1. Apparatus for Mulling Microsamples

A. Holder for vibrating tools. *a*, chuck; *b*, on-and-off switch; *c*, one type of amplitude adjustment
B. Hammer. *d*, rectangular head; *e*, shaft to fit into chuck, *a*, of holder
C. Anvil. *g*, grinding plate, brazed to base *f*

In selecting a tool holder, important considerations are a chuck, a convenient on-and-off switch, and an adjustment for selecting the proper amplitude of vibrations. Lightweight holders, weighing about 0.5 pound and intended chiefly for light marking purposes, are suitable for mulling the microquantities discussed here. These should be distinguished from heavier holders (exceeding a pound), which are awkward with the small hammer described, and are more appropriate with a hammer five or ten times as large. Satisfactory types of holders for vibrating tools are available from laboratory supply, hardware, and handicraft stores. These usually are powered by 50- to 60-cycle, 115-volt, alternating current, and function by the simple action of an alternating magnetic field. [Known sources of the lightweight holders are: Ideal Industries, Inc., 1006 Park Ave., Sycamore, Ill. (Ideal electric marker); and the Burgess Battery Co., 180 North Wabash Ave., Chicago, Ill. (Vibro-Graver).]

The anvil has a top of polished stainless steel. This is flat with edges converging to a rounded point, so that the finished preparations can readily be scraped to a heap on the projecting point for the transfer. This plate is mounted on a pipe bracket, which makes a rigid base heavy enough to resist the vibrations. The metal junctions both here and on the hammer are brazed with silver solder.

The hammer head is a small flat piece with rectangular edges adapted for scraping, and brazed to it at an angle of about 45° is a shaft that fits into the chuck of the vibrating holder. The bottom portion is stainless steel, and the upper shaft is a section of brass welding rod.

The grinder is made ready for use by inserting the shaft in the chuck and adjusting the vibrations so as to give adequate grinding without spattering. After a trial, the ear readily recognizes the intensity of the hum associated with a favorable amplitude. With the usual mulling oils, this amplitude could vary over a wide range, but it may need restricting to a low level with special media of low viscosity.

In use, a drop of mulling oil is put near the center of the anvil, and the microsample is shaken into the oil. It is important that the sample be wet by the medium; otherwise the particles would be scattered by the vibrations. The vibrating hammer is passed over the mixture repeatedly. Beneath the head, the action during each stroke is hammering, shearing, sucking, and expelling; and from 30 seconds to 2 minutes are usually sufficient to mull the mixture into a translucent and creamy consistency. Prolonged or excessively violent action may darken the preparation by emulsifying some steel, but probably metals in this state would give only a generalized absorption without specific band structure. When completed, the mull is transferred to the cell windows by scraping and dabbing motions, with the power off when touching the windows. During this step, the flat scraping edges of the hammer are utilized to concentrate the sample into a heap near the point of the anvil. To clean, the grinding surfaces are wiped with absorbent paper and rinsed with acetone, and residues on the hammer are readily loosened by rinsing with the power on.

METHOD USING REVERSED DRILL

As the vibration grinder was satisfactory, it was not necessary to develop alternatives fully. Therefore, the following method had not had extensive usage, but in tests it seemed satisfactory.

A hole is drilled partly through a metal block, and the sample and oil are mulled together in this hole by the same drill rotating in the direction opposite to its cutting direction. At a properly chosen speed, the spiral slots of the drill continuously force the sample downward to the bottom of the hole, where it is concentrated, and mulling proceeds simultaneously as centrifugal force moves the mixture in a cycle against the shearing interfaces. If the drill is reversed again, and then gently and slowly revolved by the fingers in its cutting direction as it is withdrawn, the finished mull may be recovered as two neatly concentrated heaps just within the slots near the drill tip. Some laboratory stirrers have been adapted from kitchen mixers of the intermeshing twin-blade type, and many of these have a separate socket for turning a chuck in the counterclockwise direction as required for this purpose.

DISCUSSION

The outstanding previous method for mulling microquantities consisted in grinding the sample with oil directly between the cell windows (*3*). When this is accomplished skillfully, the economy of sample and the spectral results have unquestionably been satisfactory. It is rather difficult, however, to control the spreading, thickness, and pattern of distribution consistently while grinding the sample sufficiently, and the variable results have sometimes made it expedient to tolerate poor preparations and a low quality of spectra. Unless the sample is ground previously, this method would not be applicable to hard samples, but fortunately most organic chemicals are sufficiently soft. Even with soft samples, however, the windows are scratched by contacts between themselves and may need frequent resurfacing. The vibratory method has the uniform and intensive action characteristic of mechanical methods, and is thought to be far more versatile, convenient, and dependable. It decreases the waste caused by excessive spreading and unsatisfactory spectra,

and it grinds harder substances. An outstanding difficulty in micromulling has been regathering the sample for continuing the action and for transferring, but with the vibration technique the grinding is done on flat surfaces, where simple scraping actions are effective for concentrating the sample.

The hammer described is of sufficient size to grind 2- to 25-mg. samples incorporated in a single drop of oil. Usually a drop of oil weighing from 12 to 25 mg. is shaken from a delivery tip 2 mm. in outside diameter, and the sample is then visually proportioned to this to give a creamy consistency when mulled. If the ingredients for the mull need weighing, the anvil plate can be made detachable and tared to make this easier. Larger samples can be handled, but they would spread and require an inconvenient number of grinding passes. On the other hand, smaller samples are readily ground; and the method can be adapted to very small quantities such as those appropriate for manipulations under low-power microscopes. This possibility is of interest in criminology and for electron and x-ray diffraction work.

For infrared mulls, the sample is ground in an appropriate oil that does not need removal, but if an oil-free sample is desired, the oil may be flooded off with a volatile selective solvent like hexane. Preliminary results suggest that this procedure may be useful in the preparation of samples for the potassium bromide wafer method (*8*, *9*); however, the usual advantages from grinding in an oil medium seemed to be decreaed with substances like potassium bromide and sodium chloride that fracture into cubes, probably because the surface of the cubical crystals is relatively low.

LITERATURE CITED

(1) Ard, J. S., Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, 1951, ANAL. CHEM., **23**, 680 (1951) (Abstract).
(2) Blout, E. R., and Fields, M., *J. Am. Chem. Soc.*, **72**, 479 (1950).
(3) DuBois, E., Ed., *Better Analysis*, 4 (No. 1), 6 (1953).
(4) Forziati, F. H., Stone, W. K., Rowen, J. W., and Appel, W. D., *Bur. Standards J. Research*, **45**, 109 (1950).
(5) Garlock, E. A., Jr., and Grove, D. C., *J. Am. Pharm. Assoc., Sci. Ed.*, **37**, 409 (1948).
(6) Randall, H. M., Fowler, R. G., Fuson, N., and Dangl, J. R., "Infrared Determination of Organic Structures," pp. 92–5, New York, D. Van Nostrand Co., 1949.
(7) Sands, J. D., and Turner, G. S., ANAL. CHEM., **24**, 791 (1952).
(8) Schiedt, U., *Z. Naturforsch.*, **8b**, 66 (1953).
(9) Schiedt, U., and Reinwein, H., *Ibid.*, **7b**, 270 (1952).
(10) Umbreit, W. W., Burris, R. H., and Stauffer, J. F., "Manometric Techniques and Tissue Metabolism," pp. 114, 126, 136–8, Minneapolis, Minn., Burgess Publishing Co., 1949.